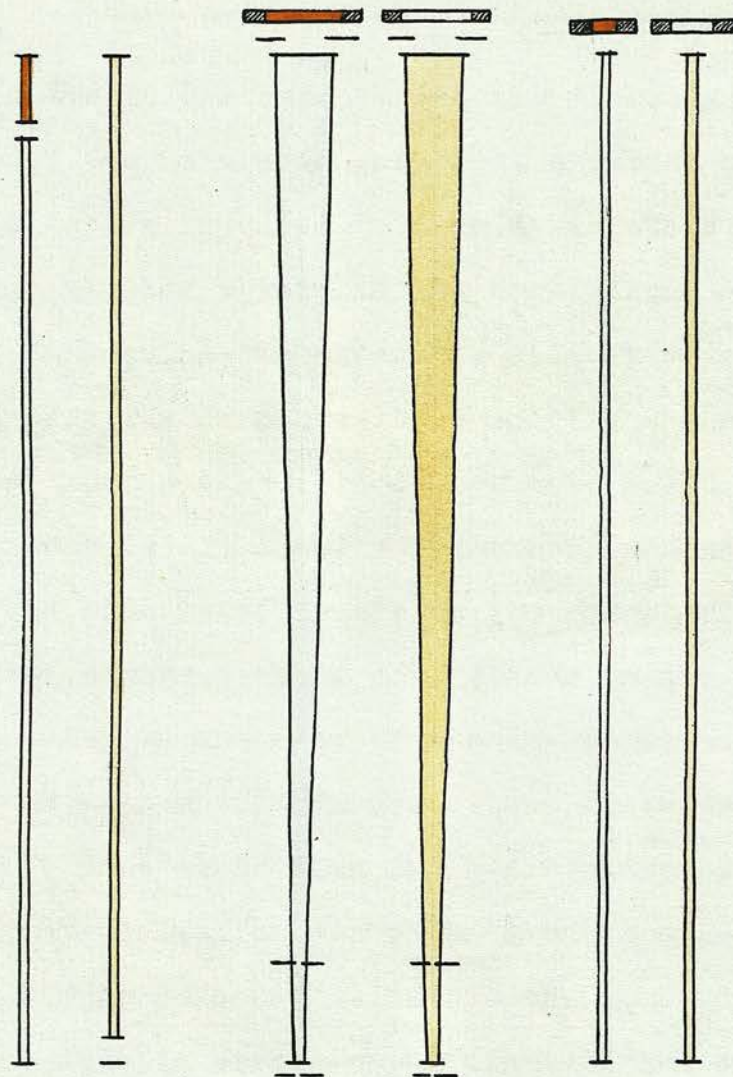


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The COLOUR ABSORPTION of SALTS and their SOLUTIONS.





Arrangement of Tubes for Preliminary Experiment. Ratio 1 to 20.

Arrangement of Cells, Troughs and Diaphragms for Large Experiment. Ratio 1 to 200.

Arrangement of Tubes and Cells for Ratio 1 to 200.

Strong Solution ■. Dilute Solution ■. Water ■.

The COLOUR ABSORPTION of SALTS and their SOLUTIONS.

Relative to the hydrate and the dissociation theories of the nature of solution, should a coloured salt dissolve in water to form a hydrate other than might already obtain in the crystalline state, it would be feasible to expect an alteration of the colour absorption of the salt on solution, and, moreover, that such a change if it occurred would be brought about in all cases where the phenomenon could be observed with possibly one or two exceptions. If, however, there were no alterations in the majority and especially in the case of the anhydrous salts it would be an argument in favour of the dissociation or at least some other than the hydrate theory.

This investigation was undertaken to ascertain whether soluble coloured salts had the same colour absorption when in strong or in dilute solution and whether in the crystalline or in the dissolved state.

Whereas the enquiry appears to be one of the simplest /

simplest, it was early found to be hedged with serious practical difficulties requiring many experiments before anything approaching accuracy could be obtained. It was decided to limit the observation to such salts as could be manipulated and observed by direct vision.

STRONG and DILUTE SOLUTIONS.

PRELIMINARY EXPERIMENTS :

In order to determine whether there was any difference in the colour absorption of strong and dilute solutions two tubes about 2.5 c.m. internal diameter were placed side by side, their ends being ground and capped. One tube was 199 centimeters long containing the dilute solution and the other was 10.1 cm. long containing the strong solution. As pure water has an appreciable colour in such a length a third tube containing a sample of the water used for solution about 189 centimeters long was placed in line with the short tube and an extra cap placed on the long tube to equalise the number of reflecting surfaces /

surfaces. A distant white screen illuminated by daylight furnished the source of light for comparing the two systems. A nearly saturated solution, or a solution of such a strength that it would allow the passage of light through, when in the short tube, was prepared and another solution of the same salt was made for the long tube so that its strength was inversely proportional to the lengths of the two tubes this being found more convenient and accurate than calibrating the tubes and introducing the substance into each in the ratio of their average diameters.

The water used for solution was very carefully twice distilled from glass vessels and allowed to settle to obtain perfect transparency. The solutions before use were also allowed to deposit sediment for twenty-four hours.

OBSERVATIONS :

Anhydrous Salts :

Potassium Bichromate :

A /

A nearly saturated solution was compared with one 19.7 times more dilute. The colour in both tubes was deep orange and there was no notable difference.

A much more dilute solution was prepared of such a strength that it appeared a bright yellow in the short tube and this was compared with a corresponding solution in the long tube 19.7 times as dilute but no notable difference was observed.

Potassium Permanganate :

Owing to the salts' high tinctorial power necessitating great dilution it showed signs of instability probably owing to a trace of organic matter and the experiment had to be abandoned.

Hydrated Salts :

Copper Sulphate :

No great difference if any. (Ratio 19.7)

Cobalt Nitrate in acid solution. Appeared to be very slightly darker in the long tube. (Ratio 19.7)

Potassium /

Potassium Ferrocyanide :

No difference was observable (ratio 19.7)

Solutions of Picric acid and of Iodine dissolved in Potassium Iodide solution were also examined but no difference could be observed.

In making these observations considerable difficulty was experienced in arriving at a definite opinion. On looking through the tubes the distant apertures were seen of very small size surrounded each by an areola of reflected light which varied in the two tubes and sometimes differed in **shade** from that of the distant apertures, while the two sets of tubes were not really optically similar and the difference of concentration of the solutions was not as great as might be.

Experiments were therefore made in such a manner and on such a scale that a definite and accurate result could be arrived at.

Detailed Experiments :

The apparatus used for this experiment consisted of two cells 15 c.m. broad and 18 c.m. deep and about
10 /

10 m.m. long and two conical troughs about 2,000 m.m. long with a 12 c.m. diaphragm at one end, and a 1 c.m. diaphragm at the other, placed parallel to each other with the cells at the far end. Ebonite diaphragms were also made to dip into the solution. The systems were mounted in a darkened room, with their ends projecting through holes in shutter, and daylight was reflected in from a large screen placed at a distance in the open so as to secure equality of illumination. The cells consisted of plates of glass held apart by thick strips of glass which had been carefully measured by micrometer, and paraffin wax was used as the cementing material. The distance of the two plates apart was determined by inserting short metal rods of different lengths between them until a sliding fit was obtained and determining by micrometer the length of the rod which fitted.

The troughs consisted of plates of ground glass, the ground surface forming the interior (to reduce the internal reflections), supported and bedded in paraffin wax, which was again supported in a water-tight trough or casing. The edges of the end-glass plates were /

were also embedded in paraffin wax made water-tight by india-rubber solution, the length being first determined by placing a steel bar, which had been filed and ground to 2,000 m.m. length, measured from a standard metre measure, in the axis of the trough and fixing the end plates so that they were in contact with the end of the bar.

Care also was taken to see that the corresponding pairs of end glass plates in the two systems were cut from the same piece of glass, so that the two systems should as far as possible be optically identical.

Both troughs and cells placed in position were filled with distilled water and compared, but both gave exactly the same shade.

The distilled water and solution for the troughs were supported above the troughs where they were allowed to settle and then syphoned off into the troughs for observation.

Accurate measurements were made of the length of one trough of one system and of one cell of the other both being filled with water. Several measurements of the cell were taken, the average being 10.198 m.m. while /

while the length of the trough was found to be 2,000.03 m.m. This gives a ratio of 196.1. Eighty grams of Bichromate to the litre form a nearly saturated solution but as twenty-five litres of the dilute solution had to be prepared, it was found more convenient to take 80.01 grams to the litre for the strong solution and 408 grams to the litre for the weak solution.

Sixty litres of water were carefully distilled in a metal still in the ordinary manner, except that the steam was washed by passing through an intermediate vessel, and the water was mixed in a large vessel to render it homogeneous, and then allowed to settle before using. The troughs and cells after thorough cleaning and polishing were filled with Bichromate and water as indicated, and several observations made at intervals to prevent wearying of the eye. The result was that just the slightest difference could be made out, the strong solution being if any the darker, but on placing both cells in front of the troughs absolutely no difference could be seen. The troughs were emptied and the cell containing the strong solution of Bichromate was taken to pieces, put together again and remeasured. The average length was 10.185 m.m. giving a ratio of 196.3, and a new strong solution was prepared containing 80.114 grams of Bichromate to the litre.

An observation was made, the same diluted solution being used as before, but this time absolutely no difference could be detected.

A third experiment was made by remeasuring the cell and preparing a new strong solution. The ratio proved to be the same, and a solution of the same strength was made, but no difference could be detected.

In these observations there was no difficulty in comparing the solutions, as, owing to the large size of the distant aperture, the absence of reflections and the use of diaphragms to limit the field, there were no disturbing elements as with glass tubes. I have therefore no hesitation in stating that there is no difference in the color absorption of Bichromate of Potash whether in strong or in very dilute solution.

SULPHATE of COPPER :

A saturated solution of Sulphate of Copper was compared with a dilute solution (ratio 196,3). It was observed that there was a marked difference between the two solutions. The strong solution was of the usual indigo blue, but the dilute solution was of a /

a pale greenish-blue colour. It was thought that basic salt might have been precipitated during the time necessary to make up and handle so large a quantity of solution. Accordingly, the glass tubes were reverted to for comparison, as in the preliminary experiment, except that the ratio was now 195.7 and that two short and two long tubes were used, as in the large experiment.

It having been proved in the large experiment that there was no difference in Bichromate of Potash, it was used as a standard for comparison in the glass tubes. Two solutions were accordingly made in the ratio of 195.7 and introduced into the glass tubes when it was observed that the appearance of the distant apertures must only be noted, the reflected light forming the areolae not being similar.

A saturated solution of Copper Sulphate was introduced into the short tube and a dilute solution (ratio 195.7) was introduced into the long tube as soon as the salt was dissolved, the solution occupying a few minutes only, and observed. A similar result was obtained as in the large experiment. A third experiment was made with strongly acid solutions, but there was /

was no difference in the result. Owing to the marked difference in the colours of the two solutions no attempt was made to measure their relative intensities. 2

COPPER CHLORIDE :

As is well known a saturated solution of Cupric Chloride is green, but on slight dilution becomes blue. A strong blue solution was prepared and compared with a dilute solution (ratio 195.7) but both solutions had the same absorption.

COBALT CHLORIDE :

Strong solution 93.4 grams to the litre. (Ratio 195.7). Both solutions the same.

NICKEL SULPHATE :

Strong solution 100 grams to the litre. Ratio 195.7. Both solutions the same.

IODINE in POTASSIUM IODIDE :

Strong solution 2 per cent. Ratio 195.7. Both solutions the same.

POTASSIUM FERROCYANIDE :

In the case of Potassium Ferrocyanide a 10 per cent solution was used for the strong solution, with the /

the ratio 195.7, but the weaker solution was remarkably more intense in color. A rough measurement for comparison by making the dilute solution more dilute, showed that the dilute solution was about three times as absorptive as the strong solution.

The experiment was repeated starting with ^astronger solution which gave about two and a half times the absorptive power.

POTASSIUM FERRIDCYANIDE :

A 30 per cent solution was compared with one 194.7 times as weak and the dilute solution was much darker. By further diluting the dilute solution it was made out to have 3 times the color absorption of the strong solution. It was believed that the darkening of the dilute solution took some minutes and after 24 hours standing was about 4 times as dark as the strong solution.

SODIUM NITROPRUSSIDE :

An 18 per cent solution was compared with one 194.7 times as dilute but there was no notable difference between them.

CHROME /

CHROME ALUM :

A 10 per cent solution of Chrome Alum dissolved in the cold was compared with one 194.7 times as weak.

The strong solution was of the usual violet color and the dilute solution had the usual dark olive green color of the green chromium salts.

POTTASIAM CHROMATE :

A 20 per cent solution was used. Ratio 194.7. There was no notable difference.

POTASSIUM PERMANGANATE :

As strong a solution as could be used was compared with one 194.7 times as weak, special precautions being taken to prevent the introduction of organic matter. The strong solution was of the usual blue purple color and the dilute was of a pink purple, in the preliminary experiment it was of a red purple. Considering the sensitiveness of the salt to chemical action, no deduction can be made from this result, especially /

especially when it is remembered that only one part
of salt would be dissolved in 100,000 of water, ^{in the dilute solution.} After
24 hours standing a further departure in color was
observed.

CRYSTALS and SOLUTIONS.

CUTTING of CRYSTALS :

From preliminary experiments it was found necessary that the section of crystal required for comparison with the solution should be as thin as could be obtained, that it should be as transparent as possible, that, if possible, it should not be less than 7 m. m. square and that its faces should be approximately parallel. Several samples of Potassium Bichromate were examined and a pure sample was selected for experiment; this sample was so brittle that it proved to be a matter of the utmost difficulty to obtain a section. All methods of grinding using any speed resulted in the ultimate breaking of the crystals. Efforts were made to prepare agglomerate blocks by compressing /

compressing the powder moistened with water or Canada Balsam Solution at pressures of many tons to the square inch, but these proved not to be transparent. The crystals cannot be warmed without cracking, so that wax and similar bodies could not be used for supporting them while grinding, but Plaster of Paris proved efficacious. The method finally adopted was to mount the crystal in Plaster of Paris on the bed of a sliding microtome, and to very slowly scrape and cut the crystal down by means of a graver, the advancing face of which was perpendicular to the crystal and the following surface forming a very acute angle with the advancing face. It was found that the crystal had to be many times remounted during cutting and the process was frequently assisted by means of a hand-file when irregularities presented themselves. In this way it was found possible to produce a section 3 m. m. thick but by cementing a section to glass by means of Canada Balsam a section three-quarters m. m. thick was finally obtained.

Another method which was found useful for rapidly reducing some crystals to shape, was to syphon water from one vessel to another by means of a fine piece of /

of linen cloth placed over a horizontal glass plate at its highest part. By placing the crystal on the flat portion of the cloth, the under surface was dissolved away, giving a fairly flat surface which could be finished on the microtome.

No difficulty was found in cutting sections of copper sulphate, commercial bichromate of potash, or Ferrocyanide of Potash, etc., a flat sheet of sand paper being used to bring them up to shape and the final grinding being done on a moistened sheet of "focusing screen" ground glass. A stout sheet of moistened paper was used for final polishing.

METHOD of COMPARISON :

The crystals to be observed were placed on a 7 m. m. diaphragm enclosed in a metal tube and their color compared with that of a saturated solution of the salts contained in a colorimeter formed of two Nessler's tubes connected by a flexible rubber tube, the depth of the solution being varied.

The solution was also observed through a 7 m. m. diaphragm and was protected from diffused light. It must be noted, however, that it is impossible to attain anything like accuracy, owing to the imperfection and want of perfect transparency of the crystal or solution.

In /

In order however, to arrive as nearly as possible at the point of similarity, consecutive observations were made and the point of identity judged from - that point at which the solution seemed just lighter, at which it appeared the same, and at which it was just darker. The observations were made many times and to assist in equalizing the illumination and relative appearance, a flat plate of ammonia alum was occasionally placed on the diaphragm of the solution.

Orientation :

The crystal was cut in the plane which was found most convenient and as far as possible in the same plane in each set of sections. Two sections of the same thickness of Potassium Ferridcyanide were compared one cut parallel and the other at right angles to the major axis and two sections of copper sulphate one cut parallel to the principal face and the other to an end face. But in neither case could any difference be made out beyond the limits of experimental error. The sections were compared directly and indirectly with their solutions in colorimeter /

No very definite point could be fixed owing to depth of color.

On calculating these results to show the relative absorption of solid in solution per 100 units of length of crystalline solid the following results are arrived at :-

No.1	.756 m.m.	thick	97	units solid in solution
No.3	3.02 m.m.	"	93.6	"
No.4	6.07 m.m.	"	85.8	"

If the thickness be plotted against the units in solution per 100 units of length of crystal, and the average curve drawn, it will be found to come practically to 100 when the thickness is very small.

That is to say Bichromate of Potash has the same color absorptive power whether in the crystalline or in the dissolved state and that the apparent variations are due to the want of transparency and imperfections of the crystals.

Cupric /

Cupric Sulphate - Specific Gravity 2.28

Strength of solution 238.99 grams per litre.

Three sections were examined, a specially selected sample of Pure Copper Sulphate being used which was remarkably transparent.

No.1 Section	1.5 m.m. thick
Similar with	15 m.m. solution
Comparatively easy to measure	

No.2 Section	2.1 m.m. thick
Similar with	23 m.m. solution

No.3 Section	3.6 m.m. thick
Similar with	36 m.m. solution

This last was rather difficult to compare owing to its depth of color, also to its remarkable brilliancy and to being of a slightly different shade from the others.

Result per 100 units of length of crystal

No.1	1.5 m.m.thickness	105	units	solid	in	solution
No.2	2.1 m.m.	"	115	"	"	"
No.3	3.6 m.m.	"	119	"	"	"

It will be seen that we have the same phenomenon here again only on the other side of the 100 and that if an exceedingly thin and perfect crystalline section /

section were obtained, it would have the same color absorptive power whether in the crystalline or in the dissolved state.

Potassium Ferrocyanide - Sp. gr. 1.85; solution 100 grams to the litre.

Three sections were examined.

No.1 section 1.245 m.m. thick

Similar with 12 m.m. solution

No.2 section 3.048 m.m. thick

Similar with 31 m.m. solution

No.3 section 6.24 m.m. thick

Similar with 63 m.m. solution

Result per 100 units of length of crystal.

No.1	1.245 m.m.thick	-	52.1	units solid in solution
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No.2	3.048 m.m.	"	-	54.9	"
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No.3	6.24 m.m.	"	-	55.0	"
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It is obvious that there is here something different from the others, the crystal having only half the absorptive power that the strong solution has and the strong solution only a third of the absorptive power which the very dilute solution has.

Potassium /

Potassium Ferridcyanide : Sp. gr. 1.86; solution 300 parts to the litre.

Three sections were examined.

No.1 .965 m.m. thick similar with 22 m.m. solution

No.2 2.255 m.m. thick similar with 25 m.m. solution

No.3 3.439 m.m. thick similar with 34 m.m. solution

Result per 100 units of length of crystal.

No.1 .965 m.m. thick equals 367 units solid in solution

No.2 2.55 m.m. thick equals 150 units solid in solution

No.3 3.44 m.m. thick equals 158 units solid in solution.

A very striking phenomenon is here observable in that No.1 section is ^{apparently} over twice as colorific as Nos. 2 and 3 which are about the same. Accordingly No.1 section was compared with a depth of solution corresponding to 100 units of solid and to 150 units of solid /

solid and it was marked that whereas the solid had the characteristic red colour, both depths of solution had the characteristic olive yellow colour of the ferridcyanide in small bulk or dilute solution, while in the case of solutions 2 and 3 the colour was red. This is the only case where this phenomenon has been observed but it may be that as in the case of bichromates (yellow and red) chrome alum (blue and purple) and other salts which show two colours in small and greater mass respectively the colour effect is not proportional to the mass about the point of change of colour owing possibly to physiological causes. It might also be mentioned that the ferridcyanide solution was much less brilliant than the crystal.

The result here would appear to be that the strong solution has only two-thirds of the absorption of the solid.

SODIUM /

Sodium Nitroprusside::

Sp. gr. 1.686. Strength of solution 180 grams.to
the litre.

Section I. .3556 m.m. thick,
similar with 4 m.m. solution.

Section II. 1.092 m.m. thick,
similar with 10 m.m. solution.

Section III. 2.54 m.m. thick,
similar with 25 m.m. solution.

Result:

No. I.	.3556 m.m. thick	= 120	parts solid in solution
No. II.	1.092 m.m.	= .977	do.
No. III.	2.54 m.m.	= 1.05	do.

Crystals of Nitroprusside were not obtained of
sufficient size to admit of adequate comparison, but
by carefully grinding and cutting small pieces to the
same thickness about 2 or 3 m.m. area, sections were
pieced together. In the case of Section I. this con-
sisted of 4 pieces each of which was about 1 m.m.
square /

square. It was not practicable to ensure grinding such small pieces with parallel faces. Thus the maximum thickness would be registered in the micrometer, while the colour observed would be about the average. I have therefore little reason to believe that this result should be other than about 100.

It is here evident that the solid and solution have both the same absorptive power.

Chrome Alum :

Sp. gr. 1.809. Strength of solution 10 per cent.

Section 1. .9144 m.m. thick,

similar with 23 m.m. solution.

Section 2. 1.143 m.m.

similar with 29 m.m. solution.

Section 3. 1.702 m.m. thick,

similar with 36 m.m. solution.

Result :

No. 1. .9144 m.m. thick = 131 units solid in
solution.

No. 2. 1.143 m.m. thick = 140 do.

No. 3. 1.702 m.m. thick = 120 do.

In this case as in the case of Ferridcyanide
the /

the solution shows two colours and was much less brilliant than the Crystal.

The Crystal would appear to have more absorptive power than the solution.

Cobalt Chloride :

Nickel Sulphate :

In the case of Cobalt Chloride three sections were prepared from masses of the salt; and in the case of Nickel Sulphate two built sections from Crystals grown in the cold containing seven molecules of water. But no numerical comparison could be made as the solution of Cobalt was brick-red and that of the solid pink-red, while in the case of Nickel the solid was blue-green, while the solution was green.

In the case of Potassium Chromate a workable section has not as yet been obtained.

Much /

Much more work could of course be done, such as, comparing solutions at several intermediate ratios, comparing crystals and solutions in light already colored by the solution etc., the comparison of bromine with its solution and the examination of the colored radical when combined with different radicals. But the evidence adduced is sufficient to show that Bichromate of Potash and Sodium Nitroprusside undergo no alteration in color absorption when dissolved in water and when largely diluted; that copper sulphate undergoes no change on solution, but that various changes of color absorption are liable to occur at any stage of the gradual addition of water to a salt, and are determined by the chemical properties of the salt, and that there is no sustained evidence to show that there is any alteration of the color absorptive power of a salt determined by its having gone into a state of solution.





















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The subjoined diagram gives a graphic representation of the changes observed. The vertical arrow means no change, the arrow pointing to the left indicates a slowing of the light vibrations or a loss of tinctorial power, and when pointing to the right a quickening or a gain in tinctorial power.

J. Rymer Patterson.

A D D E N D U M.

A method of obtaining sections which cannot be ground thin enough, e.g., Permanganate, is at present under trial, namely, to grow a film of the colored salt on a isomorphous colorless crystal. It is hoped that the method may prove successful. Failing this, however, the salt might be grown with an isomorphous colorless salt as a diluent before cutting a section. These methods will require some time for complete investigation.

GRAPHIC SUMMARY

	$K_2Cr_2O_7$	$KMnO_4$	K_2CrO_4	K_3FeCy_6
Crystal				
Strong Solution				
Dilute Solution				
	$CuSO_4 + 5H_2O$	$CuCl_2 + 2H_2O$	$CoCl_2 + 6H_2O$	$NiSO_4 + 7H_2O$
Crystal				
Strong Solution				
Dilute Solution				
	Chrome Alum $24H_2O$	$K_3FeCy_6 + 3H_2O$	Na Ntrprus $4H_2O$	Iodine (in KI)
Crystal				
Strong Solution				
Dilute Solution				